A Nickel(II) Complex with a Rigid Sexadentate Ligand

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IN a classic example of the design of multidentate chelating agents, Lions and Martin[1] prepared the iron(II), cobalt(II), and cobalt(III) complexes of sexadentate Schiff bases derived from 1,3,5-triaminocyclohexane. No ligand-field spectra or optical resolutions were reported to substantiate the proposed octahedral structures for the chelates. We have re-investigated of these complexes to determine whether the rigid ligands produce unusual co-ordination geometries with first-row transition-metal ions. Recently it has been observed[2,3] that the triamine preparation[1] yields two isomers, *cis,cis-* and *cis,trans*-1,3,5-triaminocyclohexane, the latter being unsuited for the preparation of sexadentate chelates. We have accordingly separated these isomers by preferential complexing with nickel(II) ions prior to condensation with an aldehyde.

Initially we have prepared the nickel(II) complex of *NN'N"*-tris-(2-pyridylmethylene)-*cis,cis*-1,3,5-cyclohexanetriamine (py$_3$tach). The deep red crystalline compound is formulated as [Ni(py$_3$tach)](ClO$_4$)$_2$,H$_2$O on the basis of analytical and i.r. spectral data. The magnetic moment of the complex is 3·06 B.M. (Faraday method). The electronic spectrum of the complex is summarized in the Table.

Electronic spectrum of [Ni(py$_3$tach)]$^{2+}$

	ν(cm.$^{-1}$)	ε
Dimethyl sulphoxide solution..	11,100	27·0
	12,100	26·6
	19,400	52·8
Solid (Nujol mull)	11,100	—
	12,100	—
	19,600	—

An assignment of the two components of the low-energy band based on an octahedral model[4] would attribute one component to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition and the other to the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition, enhanced *via* spin-orbit coupling. Busch and his co-workers[5] have assigned the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in tris-(α-di-imine)nickel(II) complexes at approximately 12,700 cm.$^{-1}$, and the spin-forbidden transition at lower energy. If this relative ordering of the transitions is adopted for [Ni(py$_3$tach)]$^{2+}$, the spin-forbidden transition is assigned to the dominant component of the absorption band. A reversal of this assignment gives a 10 Dq value for the sexadentate complex out of line with other ligands containing the same donor atoms. Further evidence against the octahedral model is given by the abnormally high absorptivities observed for $[Ni(py_3tach)]^{2+}$ which indicate the donor atoms no longer occupy essentially octahedral co-ordination positions. The values for ϵ_{max} of the low-energy band in tris-(α-di-imine)nickel(II) complexes are invariably less than ten.[4,5]

An alternative interpretation, based on the trigonal symmetry group, C_{3v}, assigns the two low-energy bands as transitions from the ^3A ground term to the $^3A + {}^3E$ components of the $^3T_{2g}$ octahedral term. Such trigonal splitting is not normally observed for tris(bidentate)nickel(II) complexes[6,7] and suggests a large trigonal distortion is present in $[Ni(py_3tach)]^{2+}$.

In both assignments the other observed band has its origin in the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ octahedral transition. The remaining ligand-field transition is observed by the onset of charge-transfer bands.

(*Received, May 31st, 1968; Com.* 714.)

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